(19) Federal Republic of Germany

(12) Unexamined Patent Application

(11) **DE 29 51 348 A1**

(51) Int. Cl.[3]
D 08 N 3/06

(21) File No. P 29 51 348.2

(22) Filing Date: 12-20-79

(43) Date Opened to Public Inspection: 7-2-81

(71) Applicant: Bayer AG, 6000 Leverkusen DE;
Graboplast, Györ, HU

(72) Inventors: **Salamon,** Manfred, Dr.; **Hagebaum**, Hans-Jürgen; **Wendel**, Martin, Dr., 4047 Dormagen, DE;, **Egry,** Tomas, Dipl. Ing., **Szabo**, Ilona, Györ, HU

(74) Agent: Peters, G., Patent Attorney, 6000 Leverkusen

(54) # Process for Producing a Synthetic Leather with a Coated, Smooth and Suede-like Surface

German Federal Printing Office, Berlin 06.81 130 027/206 7/70

PATENT CLAIMS

1. Process for producing a synthetic leather by forming a nonwoven fabric from staple fibers, whereby the fibers are opened on a carding machine or a pneumatic nonwoven fabric unit, the nonwoven fabric is formed, compressed, preferably needled, optionally shrunk, impregnated with a binder, optionally split, optionally ground, roughened, brushed and optionally coated, characterized in that the nonwoven fabric consists at least in part of fibers impregnated with a hydrophobing agent.

2. Process according to Claim 1, characterized in that the fibers rendered hydrophobic contain the hydrophobing agent in an applied quantity from 0.01 to 5% and preferably from 0.1 to 2%.

3. Process according to Claims 1 and 2, characterized in that the hydrophobing agent used is an oil, fat, fatty acid salt, silicone, silicone-containing product or a mixture thereof.

4. Process according to Claims 1 to 3, characterized in that a fiber mixture of fibers rendered hydrophobic and fibers not rendered hydrophobic is used to form the nonwoven fabric.

5. Process according to Claim 1 to 4, characterized in that before impregnation the nonwoven fabric is at least in part rendered hydrophobic.

6. Process according to Claims 1 to 5, characterized in that the nonwoven fabric has a sandwich structure and that the individual layers contain fibers that at least in part are rendered hydrophobic.

7. Process according to Claim 6, characterized in that it contains only one layer that in part is rendered hydrophobic.

8. Process according to Claims 1 to 7, characterized in that the nonwoven fabric consists of two nonwoven layers of which only one contains fibers that at least in part are rendered hydrophobic and that the needling of the two layers is accomplished at least during the last needle pass, that the needles enter only from the side containing the fibers that have been rendered hydrophobic, and that the needle penetration depth is chosen so that on the layer facing away from the needle entry side and free of hydrophobing agent, fiber tufts are pushed through and after roughing and brushing give rise to a suede.

9. Process according to Claims 6 to 8, characterized in that the individual layers consist of fibers with different swellability.

10. Process according to Claims 1 to 9, characterized in that the fibers rendered hydrophobic are present in the nonwoven fabric in an amount of 5 - 100% and preferably 5 - 90%.

Bayer Aktiengesellschaft

5090 Leverkusen-Bayerwerk
Central Division
Patents, Trademarks and Licenses

Dn/Wi December 18, 1979

GRABOPLAST
9002 Györ, Hungary

PROCESS FOR PRODUCING A SYNTHETIC LEATHER WITH A COATED, SMOOTH OR SUEDE-LIKE SURFACE

The invention relates to a process for producing a nonwoven fabric-based synthetic leather with outstanding softness, flexibility and other natural leather-like properties, for example high water absorbability and high water and air transport properties.

It is known to make synthetic leather or leather replacement materials based on nonwoven fabrics. To this end, nonwoven fabrics made from staple fibers or continuous filaments of synthetic or man-made materials are needled, impregnated with a latex or polyurethane product, cured or coagulated, optionally split and, depending on the intended use, coated with known coating compositions and finished. As a rule, these materials are characterized by low flexibility and poor draping.

It is also known that the softness and hand of a nonwoven fabric - and the same is true for impregnated nonwoven fabric bases for synthetic leather - is determined by the number of bonding points between the various fiber surfaces and the bonding agent used or, in other words, by the extent of bonding agent-free fiber surface. The smaller the number of bonding points and the larger the bonding agent-free fiber surface, the greater is the mobility of the fibers within the nonwoven fabric during a flexural stress.

Moreover, it is known that the softness and hand of a nonwoven fabric base depends on the titer of the fibers. The finer the fibers used, the softer is the nonwoven fabric.

Microfibers with a filament titer of about 0.1 denier, the preparation of which is described in German Examined Patent Application DE-AS 20 23 214, yield nonwoven fabrics and synthetic leather of outstanding softness. The synthetic leather produced by the process described in that publication is based on microfibers and also has only a small number of bonding points. This is because among the microfibers, present in tufts, only the capillary fibers located in the marginal zone are bonded by the impregnating agent used, so that the capillaries located within the tufts can slide over one another in the event of exposure to a flexural stress.

This process for producing a very soft synthetic leather, however, is complicated and requires a great technical effort. This is true not only for the production of microfibers but also for the subsequent upgrading

or finishing steps to convert the needle-punched felt to the desired synthetic leather.

We have now found that a nonwoven fabric base with properties required for making synthetic leather of high flexibility and good water absorption and water transport within the synthetic leather, high fiber mobility within the nonwoven fabric, a reduced number of bonding points and large binder-free surface can be obtained in technically simple manner by making the nonwoven fabric from natural or synthetic fibers rendered entirely or partly hydrophobic or a mixture thereof, preferably in the form of staple fibers and optionally as continuous filaments.

Hence, the invention relates to a process for producing synthetic leather by forming a nonwoven fabric from staple fibers, whereby the fibers are opened on a carding machine or pneumatic nonwoven fabric-making machine, laid to form a nonwoven fabric, compressed, preferably needled, optionally shrunk, impregnated with a bonding agent, optionally split, optionally ground, roughened, brushed and optionally coated, characterized in that the nonwoven fabric contains at least in part fibers impregnated with a hydrophobing agent.

The fibers rendered hydrophobic are contained in the nonwoven fabric in an amount of 5 - 100 %, preferably 5 to 90 % and particularly 30 to 70 %.

The hydrophobing agent used can be any of the known water-repellent products, such as oils, salts of fatty acids and preferably silicones or silicone-containing products. The amount of hydrophobing agent used depends on the type of agent and on the type of fiber to be rendered hydrophobic, for example wool, cotton, polyamide, polyacrylonitrile, polyester, polypropylene, cellulose etc, and on the desired effect to be produced on the article in question.

The applied amount of hydrophobing agent is, in general, from 0.05 to 5 wt% and preferably from 0.1 to 2 wt% (based on the fiber material rendered hydrophobic).

By using, as is preferred according to the invention, a mixture of fibers with different swelling properties, it is possible to obtain fibers with a specific, graduated hydrophobing effect.

The process of the invention can be carried out, for example, in that a non-needled or preferably needled nonwoven fabric made from, for example, the abovesaid fibers or a mixture thereof, and with a fiber distribution that is constant and uniform over the entire cross-section of the nonwoven fabric, is rendered hydrophobic by a dipping or spraying method before the impregnation (for example with a latex or a polyurethane), which in and of itself is known. It can also be carried out, however, by forming the nonwoven fabric from fibers which had previously been rendered hydrophobic or from a mixture of fibers that have been rendered hydrophobic and fibers that have not been rendered hydrophobic.

Particularly preferred according to the invention is the use, as nonwoven fabric base for synthetic leather, of a

nonwoven fabric having a sandwich structure. Such a nonwoven fabric can be non-needled, but preferably is needled. To make such a sandwich, the individual layers can contain fibers of the same kind, but they can also consist of fibers of different kinds. Particularly preferred is the use of fibers with different swelling properties. In this manner, the desired properties of the nonwoven fabric and synthetic leather can be adjusted in a very specific manner, for example by the choice of fibers or fiber mixture, by the type and quantity of the individual layers, by the arrangement of the fiber layers relative to one another and by the kind and amount of hydrophobing agent used.

For example, if a 2-layer needled nonwoven fabric is to be produced, in which one layer consists of polyamide fibers and the other of a mixture of polyamide and viscose rayon fibers containing about 80% of viscose rayon, and this nonwoven fabric is impregnated by the dipping method with a 1 % emulsion of a silicone containing Si-H groups, dried and heated for a short time at 140 °C to induce curing, then, as a result, the water-repellent effect of the polyamide/viscose rayon layer is greater than that of the polyamide layer. During the subsequent impregnation with a known latex, the affinity of the polyamide layer to the latex is greater than that of the viscose rayon-containing layer, but lower than it would be for a layer made of polyamide fibers not impregnated with silicone. The resulting nonwoven fabric base is thus overall softer than a nonwoven fabric base without silicone impregnation and shows higher moisture transport in the synthetic leather when the polyamide fiber side is coated and the viscose rayon-containing layer represents the inside of the leather.

The water vapor absorption of the viscose rayon is largely unaffected by the siliconizing.

By rendering hydrophobic, for example, a 3-layer nonwoven fabric so that the most hydrophilic layer is the middle layer of the nonwoven fabric, we obtain, after impregnation with a latex, a nonwoven fabric base the density of which decreases uniformly from the center toward the two sides. The nonwoven fabric base and the synthetic leather produced therefrom by coating are unusually soft so that, for example, a shoe upper leather made therefrom has pleasant wear properties. By increasing the weight of the individual layers, particularly of the described middle layer, it is then possible, by splitting the middle layer, to obtain two nonwoven fabric bases such as those described for the 2-layer nonwoven fabric construction.

A particular embodiment of the process of the invention lies in that the nonwoven fabric base used is a nonwoven fabric consisting of two layers with only one layer containing fibers that are at least in part rendered hydrophobic, that the needling of the two layers is done so that at least in the last needle pass the needles enter only from the side containing the fibers that have been rendered hydrophobic and that the needle penetration depth is chosen so that tufts of fibers devoid of hydrophobing agent are pushed through on the side opposite the side of needle entry, said fiber tufts after roughing and brushing affording a suede.

According to the process of the invention, nonwoven fabric-based synthetic leathers with an unusually soft and pleasant hand can be obtained when the impregnation with a latex binder is carried out as described in German Unexamined Patent Applications DE-OS 25 02 654, DE-OS 25 02 655 or DE-OS 26 01 781.

EXAMPLE 1

A random-fiber nonwoven fabric consisting of 60% of polyamide fibers rendered hydrophobic (about 40 mm staple length, 1.6 dtex) and 40% of polyester fibers (about 40 mm staple length, 1.6 dtex) was impregnated with an excess of latex mixture having the composition given below so that 100 g of latex mixture solids was taken up per 100 g of fiber material. The impregnated nonwoven fabric was then heated rapidly to 50 °C which caused the latex to gel. Vulcanization was then carried out with steam at 105 °C for 30 min, after which the nonwoven fabric was dried with hot air. Splitting of the nonwoven fabric gave a microporous base material for synthetic leather.

The latex mixture used had the following composition.

210.0 parts by weight of a 47% latex of a copolymer made from
- 60.0 parts by weight of butadiene
- 36 parts by weight of acrylonitrile and
- 4.0 parts by weight of methacrylic acid (= 100 parts by weight of solids)

15 parts by weight of polydimethylsiloxane, 33% emulsion
1.0 part by weight of a polyether siloxane
2.0 parts by weight of benzylphenylphenol
75.0 parts by weight of water
41.0 parts by weight of a vulcanization paste consisting of
- 2 parts by weight of colloidal sulfur
- 5 parts by weight of zinc oxide
- 1 part by weight of zinc diethyldithiocarbamate
- 5 parts by weight of titanium dioxide
- 1 part by weight of sodium diisopropyldithiocarbamate, and
- 27 parts by weight of a 5% solution of a condensation product of naphthalenesulfonic acid and formaldehyde.

The coagulation point of this latex mixture was about 40 °C.

EXAMPLE 2

A fiber mixture consisting of 70% of siliconized polyamide fibers, 1.6 dtex/40 mm, and of 30% of high-shrinkage polyester fibers, 1.3 dtex/60 mm, was carded, cross-laid and needled in the known manner with a No. 38 needle.

The nonwoven fabric weighed about 350 g/m^2, and the needling density was 750/cm^2. The nonwoven fabric was then shrunk at about 70 °C. The shrunk nonwoven fabric weighing about 450 g/m^2 was impregnated by the coagulation method with a polyurethane solution (about 50% solids deposition), coagulated, washed and dried.

The polyurethane solution had the following known composition (German Examined Patent Applications DE-AS 12 70 276, DE-AS 16 96 171:

9 kg of a dispersion of a cationic polyurethane derived from a polyester of phthalic acid, adipic acid and ethylene glycol (molar ratio 1:1:2.2), toluylene diisocyanate, N-methyldiethanolamine and 1,4-dichlorobutane, in a water/dimethylformamide [DMF] mixture, 25% in DMF

3 kg of a polyurethane made from a mixture of hexanediol polycarbonate ester and 1,4-butanediol adipate, 4,4'-diphenylmethane diisocyanate and 1,4-butanediol (25% in DMF)

0.5 kg of a polyurethane derived from adipic acid-butane diol-ethylene glycol copolyester, 4,4'-diphenylmethane diisocyanate and 1,4-butanediol (25% in DMF)

0.05 kg of magnesium chloride, 20%

0.01 kg of a commercial alum-based tanning agent

The dried material was ground and split yielding a soft suede-like synthetic leather weighing about 22 g/m^2.

EXAMPLE 3

A fiber mixture of 70% of siliconized polyester fibers, 1.6 dtex/40 mm, and 30% of high-shrinkage polyester fibers, 1.3 dtex/60 mm, was made into a nonwoven fabric by the method described in Example 2, post-treated with a polyurethane solution and processed further.

The resulting suede-like synthetic leather, about 230 g/m^2, had an obviously harder hand and was less drapable than the product obtained in Example 2.

EXAMPLE 4

A fiber mixture of 70% of siliconized polyamide fibers, 1.6 dtex/40 mm, and 30% of high-shrinkage polyester fibers, 1.3 dtex/60 mm, was made into a nonwoven fabric by the method described in Example 2, needled and shrunk.
Weight of nonwoven fabric: about 450 g/m^2
Needling density: about 800 punctures/cm^2.

a) The nonwoven fabric thus pretreated was impregnated with an approximately 23% latex dispersion

(Perbunan N 3415) at a solids deposition of about 100%, based on the weight of the nonwoven fabric, coagulated by exposure to infrared radiation, steam-vulcanized, washed, dried and then dry-heat vulcanized at 140 °C.

The crude product thus obtained was split and ground on both sides. The resulting synthetic suede leather can be died with dispersion dyes and, depending on thickness, is suitable for outer garments, cushion material or shoe upper leather.

b) The pretreated nonwoven fabric was finished with a 23% latex dispersion consisting of 50% of Perbunan N 3415 and 50% of Perbunan N Latex KA 8194 by the method described under 4a. The solids deposit amounted to 100%, based on the initial weight of the nonwoven fabric.

The split and ground material can be dyed with dispersion dyes and it has a softer, more textile-like hand than the product from a). It can be used for outer garments.

EXAMPLE 5

A fiber mixture of 70% of siliconized and 20% of non-siliconized polyamide fibers [sic - Translator] (about 8% residual shrinkage), 1.6 dtex/40 mm, was made into a nonwoven fabric by the method described in Example 2, impregnated with the latices indicated in Example 4 and processed further.

In both cases, the end products were softer than those from 4a and 4b and showed better strength, tear strength and stitch tear strength.